UNITED STATES DEPARTMENT OF COMMERCE
HENRY A. WALLACE, Secretary
NATIONAL BUREAU OF STANDARDS
Lyman J. Briggs, Director

✦

Journal of Research

of the

National Bureau of Standards

✦

Volume 35, Number 2
August 1945

[Published with approval of the Director of the Budget]

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1945

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Washington 25, D. C. - Price 30 cents, $3.50 per year on subscription

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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available. An order blank is available on the last page of this issue.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1664

Part of Journal of Research of the National Bureau of Standards, Volume 35, August 1945

MASS SPECTROMETRIC ANALYSES OF HYDROCARBON AND GAS MIXTURES[1]

By A. Keith Brewer and Vernon H. Dibeler

ABSTRACT

The basic principles underlying mass spectrometric analysis of hydrocarbon and gas mixtures are outlined. The method of calculating the composition from the mass-abundance records is described. Analyses of a number of hydrocarbon and other gas mixtures are shown. Whenever possible, comparisons with different methods of analyses are given. The reproducibility and the accuracy obtainable in mass spectrometric analyses are described.

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I. INTRODUCTION

The basic principles involved in the mass spectrometer were worked out as early as 1910 by Sir J. J. Thomson. The first mass spectrographs utilizing these principles, much as in the present-day instrument, were built by Aston and by Dempster about 1920. In spite of this early conception, it is only within the last 2 years that the mass spectrometer has been developed to the point where it is capable of making precise analyses of gas and hydrocarbon mixtures.

This new development has been made possible, not from changes in principle or basic design, but from the discovery that hydrocarbon molecules upon bombardment at low pressures (10^{-5} to 10^{-6} mm) by electrons having 50 or more volts of energy are dissociated into all possible disintegration fragments.[2] The ratios in which the fragments occur are the same over a wide pressure range for each molecular species but are never the same for different species. The development of sensitive electronic pick-ups and automatic-recording mechanisms has not only contributed to the ease of operation but has made possible a speed and precision that could not be attained by manual controls.

[1] This work was financed in part from funds made available by the Rubber Reserve Co.

[2] H. Hoover, Jr. and H. W. Washburn, Calif. Oil World Petroleum Ind., (Nov. 1941); H. W. Washburn, H. F. Wiley, and S. M. Rock, Ind. Eng. Chem. Anal. Ed. **15**, 541 (1943); H. W. Washburn, H. F. Wiley, S. M. Rock, and C. E. Berry, Ind. Eng. Chem. Anal. Ed. **17**, 74 (1945).

This paper describes briefly the method by which chemical composition can be determined from mass spectrometric records, the types of mixtures that are being analyzed, and the reproducibility that is being realized. Representative analyses made in the mass spectrometer laboratory at the National Bureau of Standards by the use of a mass spectrometer manufactured by the Consolidated Engineering Corporation are cited to illustrate the applicability of the instrument.

II. DESCRIPTION OF THE MASS SPECTROMETER

In the mass spectrometer, molecular masses are separated by virtue of differences in their momenta when all have been given an identical kinetic energy in a given direction. Four steps are involved in the separation.

First, the molecules are given a positive charge. This is accomplished in the instrument by bombardment with a stream of 50-volt electrons, the electron current being about 5 microamperes. The gas pressure in the ionizing chamber is of the order of 10^{-5} millimeter. The filament is placed outside the ionization chamber, where the gas pressure, as measured on an ionization gage, ranges from 10^{-7} to 10^{-6} millimeter. This insures long filament life and prevents products of molecules cracked on the hot filament from reentering the ionizing chamber.

Second, the ions are given an identical kinetic energy along a given path by a potential difference between two accelerating slits. In the instrument this potential can be manually or automatically varied from 4,000 to 200 volts. The kinetic energy of the ions is given by $1/2\ mv^2=eE$, where m is the ion mass, v the velocity, e the charge on the ion, and E the accelerating potential.

Third, the ions are resolved in a uniform magnetic filed by being deflected in arcs whose radii are proportional to their momenta. The instrument is of the 180-degree focusing type, the entire resolved ion path being within the uniform magnetic field of a large electro magnet.

The centripetal force deflecting the ions is balanced by centrifugal force, as expressed by $Hev=mv^2/r$, where H is magnetic field strength and r is the radius of deflection. Dividing both sides by v and rearranging, the above expression gives $mv=Her$; this shows the radius to be proportional to the momentum. Substituting the energy value for v in the momentum equation, the basic expression for the principle of the mass spectrometer is obtained as $(m/e)=(H^2r^2)/2E$. Expressing all values in practical units this equation becomes

$$Hr=\left[\frac{2\times1.66\times10^{-24}\times mV}{4.803\times10^{-10}\times300}\right]^{1/2}\times3\times10^{10}=144.00\sqrt{m}\sqrt{V},$$

where H is in gauss, V in volts, r in centimeters, and m in units of hydrogen atoms.

Fourth, the resolved ion beams are collected and recorded. In the instrument the focusing radius, r, is fixed at 12.7 centimeters. The various masses are made to pass over the collector slit by varying V while H is kept constant. This is accomplished by permitting the charge on the ion-accelerating slit to leak to ground through a high resistance. As the potential decreases a progression of masses from light to heavy is brought to focus on the collector slit. The arrangement chosen has the advantage of providing a nearly linear record as

the radius of the ion path varies as the square root of the mass, whereas the rate of potential leak is inversely proportional to the voltage.

The resolved ion masses are collected and the ion current is amplified by a direct-current feed-back amplifier. The output is fed through four galvanometers in series. Shunts are provided to reduce the sensitivity of the second, third, and fourth galvanometers to one-third, one-tenth, and one-thirtieth that of the first. This gives the 8-inch-wide recording paper an effective width of 240 inches. The deflections of the four galvanometers as well as the scale divisions are photographed simultaneously on the moving record.

A mass marker is provided to make possible the easy identification of the various mass numbers. The marker consists of a relay that trips at definite intervals to throw a spot of light on the moving record when the acceleration potential passes fixed multiples of a chosen reference voltage.

III. MASS SPECTRA OF HYDROCARBON MOLECULES

The ionization potentials of hydrocarbon molecules range from about 9 to 14 volts. The 50-volt ionizing electrons possess enough energy not only to ionize the molecules but also to dissociate them into all possible fragments. As sufficient molecules are ionized for the probability laws to hold, the fragments of each molecular species always occur in the same abundance ratio.

In table 1 are given the cracking patterns for some of the C_4 hydrocarbons.

TABLE 1.—*Mass spectrometer calibration patterns*

m/e	n-Butane	Isobutane	Butene-1	*cis*-Butene-2	*trans*-Butene-2	Isobutene	1,2-Butadiene	1,3-Butadiene	Ethyl acetylene
24	Trace	0	0.21	0.12	0.11	Trace	0.32	0.44	0.45
25	1.61	3.03	2.07	1.24	1.24	0.69	2.42	3.29	2.59
26	46.95	72.73	23.94	16.77	16.43	8.57	14.31	24.70	12.51
27	283.03	959.60	73.65	50.78	51.59	36.05	40.10	63.70	36.77
28	240.85	106.46	64.54	47.58	49.34	37.23	25.46	39.50	31.24
29	297.76	215.15	27.34	22.33	28.56	18.16	.72	.88	1.23
30	6.65	5.45	1.91	1.31	1.23	1.24	.03		
31			.04	.04	.04				
36	.25	1.21	.44	.22	.20	.32	.74	.90	1.01
37	6.71	35.76	6.81	3.71	3.64	5.31	5.08	5.85	7.99
38	14.63	86.76	11.88	6.86	6.54	11.38	7.39	7.85	14.78
39	112.20	658.59	88.65	59.69	58.99	84.87	39.15	95.25	77.26
40	15.75	99.80	17.18	11.31	11.24	20.78	1.34	3.29	2.58
41	205.28	1444	228.19	162.21	166.01	187.23		.13	.03
42	92.53	1208	7.93	5.32	5.47	6.67			
43	734.76	3666	.06	.12	.07	.07			
44	24.14	118.79							
45	.30	1.41							
48	.15	Trace	.44	.29	Trace	.22	1.12	1.22	1.13
49	1.78	4.04	2.89	2.21	2.25	1.82	6.24	6.99	6.49
50	7.62	22.22	10.59	9.16	9.44	8.33	21.56	23.31	20.68
51	7.52	23.03	9.84	8.98	9.30	7.91	19.82	21.21	18.30
52	2.08	5.45	3.35	3.07	3.14	2.22	10.60	10.77	7.91
53	6.66	20.00	12.84	12.59	13.65	9.49	37.91	55.52	41.67
54	1.98	3.23	6.63	6.72	6.29	4.52	100.00	100.00	100.00
55	7.42	16.57	40.69	37.81	38.76	31.28	4.30	4.30	4.30
56	6.20	13.94	100.00	100.00	100.00	100.00	.07	.07	.07
57	19.21	110.30	4.31	4.31	4.31	4.31			
58	100.00	100.00	.07	.07	.07	.07			
59	4.35	4.35							
60	.07	.07							
SENSITIVITY									
(d/μ)	3.86	0.89	11.15	12.77	12.97	14.01	19.11	16.76	19.50

In preparing table 1 the abundance of the base mass was assigned an arbitrary value of 100; and the abundance of all other masses weighted accordingly. The base mass is that of the normal molecule composed of C^{12} and H atoms. The only heavier peaks observed are those due to the heavy isotopes, C^{13} and D. No association between molecules is detected at the pressure existing in the analyzing chamber.

The sensitivity for each compound is given at the bottom of the table. Sensitivity is defined as the number of divisions of base peak per micron of gas pressure. As the peaks are proportional to the pressure over the range in which the instrument is operated, the sensitivity is independent of the sample pressure or of the partial pressure of any constituent present.

The isotopic contribution to successive peaks is shown in table 2.

TABLE 2.—*Isotope correction factors*

Positive ion	m/e	(m/e)+1	(m/e)+2
		Percent	*Percent*
C	12	1.051	0
CH	13	1.066	1.6×10^{-4}
CH_2	14	1.081	3.2×10^{-4}
CH_3	15	1.096	4.8×10^{-4}
CH_4	16	1.111	6.4×10^{-4}
C_2	24	2.102	0.011
C_2H	25	2.117	.011
C_2H_2	26	2.132	.012
C_2H_3	27	2.147	.012
C_2H_4	28	2.162	.012
C_2H_5	29	2.177	.013
C_2H_6	30	2.192	.013
C_3	36	3.153	.033
C_3H	37	3.168	.034
C_3H_2	38	3.183	.034
C_3H_3	39	3.198	.035
C_3H_4	40	3.213	.035
C_3H_5	41	3.228	.036
C_3H_6	42	3.243	.036
C_3H_7	43	3.258	.036
C_3H_8	44	3.273	.037
C_4	48	4.204	.066
C_4H	49	4.219	.067
C_4H_2	50	4.234	.068
C_4H_3	51	4.249	.068
C_4H_4	52	4.264	.069
C_4H_5	53	4.279	.069
C_4H_6	54	4.294	.070
C_4H_7	55	4.309	.071
C_4H_8	56	4.324	.071
C_4H_9	57	4.339	.072
C_4H_{10}	58	4.354	.073

The C^{13} and D contributions for the ions given in column 1 (table 2) to the peaks 1 and 2 mass units higher ($m/e+1$ and $m/e+2$) are computed on the basis of the observed abundance of C^{13} as 1.051 percent and D as 0.02 percent.

The masses given in Table 1 are due to singly charged ions. In addition to these, peaks are observed for doubly charged ions, for ghosts, and for "labile" groups, principally hydrogen. In the case of *n*-butane, for instance, the singly charged ions constitute 99.69 percent of the total. The percentage of doubly charged ions is higher for unsaturated hydrocarbons and for diatomic molecules.

Only singly charged ions are used in computing the composition from a mass record. The presence of other ion groups introduces no complication as they occur in proportion to the pressure and are easily distinguished. They are in fact often a help in characterizing the parent molecule.

A mass record for a typical gas mixture is shown in figure 1.

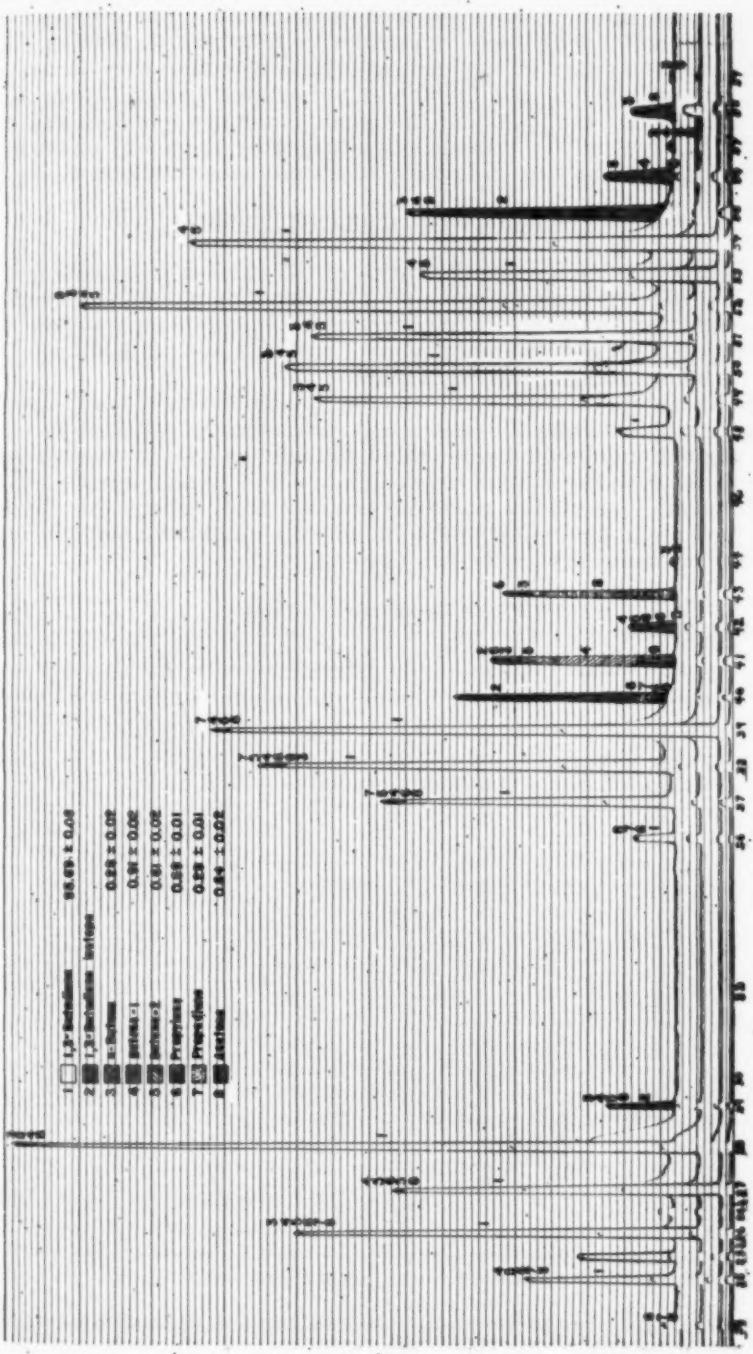

FIGURE 1.—*Mass record for a typical gas mixture.*

The record has been illuminated to show the contributions to the various mass numbers made by each constituent. The traces of the four galvanometers decrease in sensitivity from top to bottom. To obtain the abundance of the various masses it is necessary to correct the observed peak height for the galvanometer tracing used. The highest galvanometer peak on the paper is always selected, and the number of divisions it subtends is multiplied by the shunt in order to express the peak heights in terms of the most sensitive galvanometer.

METHOD OF CALCULATION

Both the base peaks and the ratios of the various fragments in the cracking patterns must be considered in analyzing a mass spectrogram like that shown in figure 1. In consequence, it is necessary to have the cracking pattern and the sensitivity of each compound that might be present before making the calculation.

The procedure can best be illustrated by considering a simple hydrocarbon mixture having the pattern given in column 2 of table 3. The values given represent the relative abundance of the various ions recorded at each mass listed in column 1. The records are all read to 0.1 division. All masses observed are recorded, except those below 24, which are not essential to the calculation when methane, nitrogen, and carbon monoxide are known to be absent.

TABLE 3.—*Mixture analysis*

m/e	Mixture	*n*-Butane	Isobutane	1-Butene	2-Butene	Isobutene	1, 3-Butadiene	1, 2-Butadiene	Residuals
24	4.7			0.05	0.04		4.64	0.02	−0.05
25	35.9	0.03	0.04	.52	.43	0.01	34.66	.13	.08
26	275.1	.98	.93	6.00	5.73	.20	260.25	.75	.26
27	728.6	5.89	12.28	18.26	17.66	.83	671.18	2.11	.39
28	457.8	5.01	1.36	16.14	16.72	.86	416.19	1.34	.18
29	34.3	6.19	2.75	6.84	8.78	.42	9.27	.04	.01
30	1.2	.14	.07	.48	.44	.03			.04
36	9.8	.01	.02	.11	.07	.01	9.48	.04	.06
37	65.6	.14	.46	1.70	1.27	.12	61.64	.27	
38	90.0	.30	1.11	2.97	2.31	.26	82.71	.39	−.05
39	1,061.0	2.33	8.43	22.16	20.47	1.95	1003.60	2.06	
40	44.8	.33	1.28	4.29	3.89	.48	34.67	0.07	−.04
41	142.1	4.27	18.49	57.05	56.62	4.31	1.37		−.03
42	21.5	1.92	15.46	1.98	1.86	.15			.13
43	62.4	15.28	46.93	.02	.03				.14
44	2.0	.50	1.52						−.02
48	13.1			.11	.10	.01	12.85	.06	−.03
49	75.6	.04	.05	.72	.77	.04	73.65	.33	
50	253.2	.16	.28	2.65	3.21	.19	245.61	1.13	−.03
51	230.8	.16	.29	2.46	3.15	.18	223.48	1.04	.04
52	116.1	.04	.07	.84	1.07	.05	113.48	.56	−.01
53	595.4	.14	.26	3.21	4.53	.22	584.99	1.99	−.06
54	1,063.0	.04	.04	1.67	2.25	.10	*1053.65*	*5.25*	
55	69.9	.15	.21	10.17	12.95	.72	45.31	.23	.16
56	62.8	.13	.18	*25.0*	*34.5*	*2.3*	.74		−.05
57	4.5	.40	1.41	1.08	1.49	.10			.02
58	3.4	*2.08*	*1.28*	.02	.02				.01
59	.2	.09	.06						.03
[a] S		3.86	.89	11.15	12.87	14.01	16.76	19.11	Total:
μ		.54	1.44	2.24	2.68	.16	62.87	.27	70.20
Percent		.77	2.05	3.19	3.82	.23	89.56	.38	100.0

[a] S=sensitivity; μ=micron of pressure.

Several methods can be used in separating the various components of the gas mixture. The one described herein is the principal procedure used at the National Bureau of Standards. It consists in re-

moving mathematically the contribution of the various constituents from each mass number. When possible each compound is subtracted individually starting with the highest masses.

A survey of the pattern in column 2 shows clearly that no hydrocarbons are present heavier than butanes of base mass 58; the 59 peak can be accounted for fully by the heavy isotope contribution from 58. The first problem is, therefore, to determine if 58 is due to *n*-butane, to isobutane, or to both. Table 1 shows that *n*- and isobutanes make very different contributions to the 43 peak. As the 44 peak is the correct size for the isotope contribution from 43, propane and carbon dioxide are shown to be absent. In consequence, the only contributors to 58 and 43, other than butanes, are the second isotopes from 56 and 41; these contributions are 0.05 and 0.04 division, respectively.

The relative contribution of *n*- and isobutanes to the 58 and 43 peaks are expressed by the simple linear equations as

43 peak=7.3476 *n*-butane+36.6667 isobutane=62.35 divisions
58 peak=1.00 *n*-butane+1.00 isobutane = 3.36 divisions.

These can be solved by determinants as follows:

$$n\text{-Butane}=\frac{\begin{vmatrix}62.35 & 36.67\\ 3.36 & 1.00\end{vmatrix}}{\begin{vmatrix}7.347 & 36.67\\ 1.00 & 1.00\end{vmatrix}}=\frac{-60.85}{-29.3191}=2.08 \text{ divisions.}$$

Similarly, isobutane=1.28 divisions. These values appear in columns 3 and 4 at mass 58. When the two base peaks are multiplied by their respective patterns the contribution of the two butanes to all the masses is obtained and can be subtracted out.

The second step is to remove the butanes shown to be present by the large 56 peak. For sake of simplicity 2-butene will be considered as an equimolar mixture of *cis*- and *trans*-isomers. The procedure is the same as that followed for the butanes, but three equations are needed as three butenes are possible. Table 1 shows that with reference to the base peak, the peaks at 55 and 41 are markedly different for the butenes. The only possible remaining compounds tha can contribute to the 55 and 56 peaks are the isotopes from 1, 3-butadiene and ethyl acetylene. Possible remaining contributors to 41 are propenes and the isotope from methyl acetylene.

The approximate nonbutene contributor to the three peaks is first determined; this is later corrected to fit the equations. Propene, having a base peak of 42, can be determined quite accurately on the first approximation. The butene contribution to 42 is small and does not differ greatly for the three butenes. Taking an average contribution for the butenes, the size of the 42 peak can be calculated from the 56 peak. In the present case the entire 42 peak can be accounted for by butenes, hence only a trace of propene can be present. The fact that the 39 peak is almost as large as 54 indicates a large concentration of 1, 3-butadiene and a negligible concentration of ethyl acetylene. The isotope contributions to the 41, 55, and 56 peaks can now be computed from table 1; the values are 1.37, 45.71 and 0.74 divisions, respectively.

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The butenes are now separated by the following linear equations:

$$41\ \text{peak} = 2.2819B_1 + 1.6411B_2 + 1.8723B_1 = 117.86\ \text{divisions.}$$
$$55\ \text{peak} = 0.4069B_1 + 0.3754B_2 + 0.3128B_1 = 23.83\ \text{divisions.}$$
$$56\ \text{peak} = 1.00B_1 + 1.00B_2 + 1.00B_1 = 61.75\ \text{divisions.}$$

Solving by determinants,
Butene-1=

$$\frac{\begin{vmatrix} 117.86 & 1.6411 & 1.8723 \\ 23.83 & 0.3754 & 0.3128 \\ 61.75 & 1.00 & 1.00 \end{vmatrix}}{\begin{vmatrix} 2.2819 & 1.6411 & 1.8723 \\ 0.4069 & 0.3754 & 0.3128 \\ 1.00 & 1.00 & 1.00 \end{vmatrix}} = \frac{1.18}{0.0472} = 25.0\ \text{divisions.}$$

Similarly, butene-2=34.5 division and isobutene=2.3 divisions.

The above values for the butenes appear in columns 5, 6, and 7 at mass 56. The contribution of each butene can now be computed and subtracted. The remaining divisions are due to the butadienes and to possible small amounts of methyl or ethyl or vinyl acetylene and to propene. Ethyl acetylene can be shown to be present in no more than a trace as the 38 peak is 7.84 percent of the 54 peak; this is almost exactly the pattern for 1,3- butadiene. The ethyl acetylene pattern is almost twice this size.

The butadienes can now be resolved in the manner described for the butanes and the butenes by using the 54 base peak and the 39 peak. Thus

$$39\ \text{peak} = 0.9525Bd_{1,3} + 0.3915Bd_{1,2} = 1005.66\ \text{divisions}$$
$$54\ \text{peak} = 1.00Bd_{1,3} + 1.00Bd_{1,2} = 1058.90\ \text{divisions}$$

1,3-Butadiene=1053.65 divisions
1,2-Butadiene=5.25 divisions.

These values appear in columns 8 and 9 (table 3) at mass 54. The contributions of the butadienes can now be computed and subtracted. The residuals are given in column 10.

The residuals are particularly important in that they show errors in approximations as well as errors in readings and in computations. Positive residuals indicate too little estimated, whereas negative residuals indicate too much subtracted. In the present case the residuals are all small and within the limits of reading error. This indicates the correctness of the assumption that propene and the various acetylenes were absent.

The accuracy of the above assumptions can be estimated by considering the size of the residuals that would have been left had 1 percent of the various possible contaminants been present. These values would be: for propene, 18 divisions on 42; for carbon dioxide, 20 divisions on 44; for ethyl acetylene, 19 divisions on 54; for vinyl acetylene, 21 divisions on 52; and for propadiene, 11 divisions on 40. In addition, each compound would contribute to the residuals on peaks of lower mass than those mentioned. The residuals on all peaks are weighed in the final calculations.

In order to calculate the mole percent of each constituent, the number of divisions of the various components must be divided by the sensitivity. This converts divisions to microns of pressure. The sum

of all the partial pressures gives the total "computed" pressure of the sample. This pressure should be identical to the "read" pressure as given by the mercury manometer on the inlet measuring volume. The read and computed pressures, however, usually differ by a few tenths of a millimeter, due primarily to water vapor in the sample, which is adsorbed on and later desorbed from the dry glass walls of the inlet system. As water is almost always present and cannot be measured accurately, it is never advisable to compute the concentration of any component by difference. All percentages, therefore, are figured by the use of the "computed" microns as a measure of total pressure of the sample.

V. REPRESENTATIVE ANALYSES

The types of gas mixtures that can be analyzed with the mass spectrometer can best be illustrated by representative analyses made at the Bureau.

The results obtained from a series of butadiene samples are shown in table 4. Included in the table are the freezing point values for 1,3-butadiene as measured by F. D. Rossini.

TABLE 4.—*Mass Spectrometer (mole percent)*[a]

Component	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Sample 11
1,3-Butadiene	98.47±0.03	99.13±0.04	99.47±0.03	97.97±0.05	98.57±0.01	98.17±0.07
1,2-Butadiene	.38±.03	.07±.04	.09±.03	.17±.05		1.11±.08
Propadiene						.11±.01
Propylene	.87±.03		.02±.01	.03±.00	.06±.01	.06±.01
Propane	.01±.00					
1-Butylene	.09±.01	.30±.02	.15±.03	.96±.01	.93±.05	.03±.01
2-Butylene	.06±.01	.42±.03	.25±.03	.82±.01	.32±.04	.23±.01
n-Butane	.05±.01	.02±.01	.02±.01		.09±.01	.06±.01
Pentadienes					.02±.01	.11±.01
Pentenes	.01±.00					.02±.01
Vinyl cyclohexene	.05±.01	.05±.01	.05±.01	.05±.01	.03±.01	.10±.01
Total	100.0	100.0	100.0	100.0	100.0	100.0
FREEZING POINT (MOLE PERCENT)[b]						
1,3-Butadiene	98.56 ±0.08	99.16 ±0.08	99.40 ±0.08	97.99 ±0.08	98.22 ±0.08	98.10 ±0.01

[a] Limits represent maximum deviation from average of 2 independent analyses.
[b] Limits of uncertainty estimated by F. D. Rossini.

The reproducibility of independent analyses is illustrated in table 5.

TABLE 5.—*Refined butadienes*

	Cylinder 11-20			
Run number	1141A	1141B	1158	1159
Computed by	DIT	VHD	LE	DIT
Operator	HP	LP	VHD	VHD
Component:	*Mole percent*	*Mole percent*	*Mole percent*	*Mole percent*
1,3-Butadiene	98.62	98.63	98.61	98.63
Propylene	.03	.03	.03	.02
Total butenes	1.32	1.30	1.33	1.31
1-Butene	.41	.35	.49	.45
2-Butene	.91	.95	.84	.86
n-Butane	.02	.02	.02	.02
Vinyl cyclohexane	.02	.02	.02	.02
Total	100.0	100.0	100.0	100.0

Runs 1141A and 1141 B were made on the same day. Runs 1158 and 1159 were made 1 week later. The samples were withdrawn from a standard 1-quart ICC container nearly filled with liquid. The technic employed was to set the cylinder in an upright position and remove 0.4 milliliter of liquid from the bottom valve by means of a special liquid sampler, made from two small needle valves connected by a short piece of 2.0 millimeter capillary tubing. The entire quantity of liquid in the capillary was expanded into an evacuated glass cylinder, from which one or more vapor samples were withdrawn for analyses. Each analysis refers to a separate liquid sample computed on an entirely independent basis.

The reproducibility obtained in an impure sample of butadiene is illustrated in table 6. The extent to which the deviations given are due to sampling and to the instrument is difficult to tell. Errors from both sources should increase with the impurity.

TABLE 6.—*Crude butadiene*

Component	Mole percent	
1,3-Butadiene	34.80	• ±0.07
1,2-Butadiene	1.8	± .2
Propylene	.02	± .01
1-Butene	7.1	± .2
2-Butene	48.2	± .3
n-Butane	.10	± .03
Methyl ethyl ether	7.97	± .05
Total	100	

• Limits represent the deviation from the average of duplicate analyses.

This particular analysis is interesting in that it illustrates the procedure that must be followed when peaks are encountered for which no pattern is available. The sample was submitted because it contained an impurity that interfered with both the infrared and ultraviolet absorbtion analyses of butadiene. In addition to the usual impurities the pattern showed a set of peaks with primary contributions at 60, 45, and 31. These masses can only result from the fragmentation of *n*- or isopropyl alcohol, acetic acid, methyl formate or methyl ethyl ether. Each of these compounds was obtained and its pattern determined; methyl ethyl ether alone agreed with the sample pattern.

In the event that the pattern for the possible contaminants could not have been obtained, the one actually present could have been identified and its concentration estimated with a reasonable degree of accuracy. The ratio of 61 and 46 isotope peaks to the 60 and 45 peaks showed only one oxygen atom to be present. This eliminated the formate and acetic acid. The two alcohols were improbable on the basis of boiling points. The sensitivity of methyl ethyl ether, the only remaining possibility, could be estimated from analogous compounds with very little error in the final calculations.

The reproducibility and range of analyses in complex gas mixtures are illustrated in tables 7, 8, and 9.

The analyses given are representative of those obtained in copolymer plants for recycled butadiene and for the noncondensable vapors from the styrene condenser, whereas table 9 is representative of products of combustion of certain types of oil flames.

TABLE 7.—*Recovered butadiene*

Component	Mole percent
1,3-Butadiene	70.53 ± 0.04
1,2-Butadiene	4.61 ± .13
Propadiene	2.42 ± .01
Propylene	5.70 ± .10
1-Butene	13.8 ± .1
2-Butene	2.15 ± .09
n-Butane	.31 ± .01
Pentadienes	.11 ± .01
Pentenes	.050 ± .001
Styrene	.05 ± .02
Vinyl cyclohexene	.04 ± .01
Air	.18 ± .01
Carbon dioxide	.08 ± .02
Total	100

[a] Limits represent the deviation from the average of duplicate analyses.

TABLE 8.—*Noncondensible gases from styrene condenser*

Component	Mole percent
1,3-Butadiene	22.96 [a] ± 0.04
Ethylene	.73 ± .08
Propylene	.08 ± .02
1-Butene	2.99 ± .02
2-Butene	5.71 ± .01
n-Butane	.120 ± .005
Pentadienes	.013 ± .002
Pentenes	.030 ± .005
Styrene	.200 ± .005
Ethyl benzene	.005 ± .001
Vinyl cyclohexene	.140 ± .005
Nitrogen	49.9 ± .3
Oxygen	11.49 ± .02
Argon	.560 ± .001
Carbon dioxide	5.10 ± .09
Total	100

[a] Limits represent the deviation from the average of duplicate analyses.

TABLE 9.—*Oil flame fumes*

Component	Mole percent
Methane	0.48 [a] ± 0.05
Acetylene	.05 ± .01
Ethylene	.45 ± .04
Propylene	.06 ± .01
Acetaldehyde	.18 ± .02
Butenes	.02 ± .01
Benzene	.07 ± .01
Toluene	.010 ± .005
Neon	.06 ± .01
Nitrogen	77.7 ± .1
Carbon monoxide	2.91 ± .03
Oxygen	6.53 ± .06
Argon	1.10 ± .01
Carbon dioxide	10.38 ± .02
Total	100

[a] Limits represent the deviation from the average of duplicate analyses.

Two magnet settings were required in taking the record for each mixture. A magnet current of 0.5 ampere was used to sweep the mass region from 12 to 90 and a current of 0.7 ampere for the region from 90 to 150.

The reproducibility of the instrument, as well as that of the sampling technic described under table 5, is shown in table 10.

TABLE 10.—*Hydrocarbon mixture*

Liquid sample	I (3/21/45)		II (3/22/45)		III (3/22/45)	
Vapor sample	1	2	1	2	1	2
Component	*Mole percent*	*Mole percent*	*Mole percent*	*Mole percent*	*Mole percent*	*Mole percent*
Propane	3.33 ±0.04	3.28 ±0.02	3.35 ±0.01	3.31 ±0.02	3.33 ±0.02	3.35 ±0.01
1,3-Butadiene	2.56 ± .01	2.55 ± .01	2.62 ± .01	2.57 ± .01	2.53 ± .03	2.56 ± .01
Total Butenes	69.43 ± .04	69.39 ± .08	69.33 ± .03	69.43 ± .01	69.38 ± .01	69.3 ± .1
n-Butenes	21.78 ± .07	21.5 ± .4	22.8 ± .2	22.5 ± .3	22.2 ± .3	21.6 ± .3
Isobutene	47.65 ± .03	47.8 ± .3	46.5 ± .2	47.0 ± .3	47.0 ± .4	47.80 ± .05
Total Butanes	22.43 ± .05	22.5 ± .1	22.35 ± .04	22.32 ± .05	22.3 ± .1	22.40 ± .08
n-Butane	11.50 ± .01	11.62 ± .03	11.61 ± .04	11.62 ± .04	11.67 ± .01	11.7 ± .1
Isobutane	10.93 ± .02	10.92 ± .02	10.75 ± .08	10.70 ± .05	10.69 ± .08	10.63 ± .08
Total Pentanes	2.25 ± .04	2.26 ± .02	2.37 ± .06	2.37 ± .05	2.33 ± .01	2.38 ± .03
n-Pentane	1.01 ± .03	1.01 ± .01	1.04 ± .02	1.01 ± .03	1.00 ± .03	1.07 ± .03
Isopentane	1.25 ± .04	1.25 ± .03	1.33 ± .06	1.36 ± .01	1.34 ± .01	1.32 ± .05

a Limits represent deviation from the average of 2 independent analyses of the same sample withdrawn from a vapor reservoir.

Each double column headed by roman numerals refers to a liquid sample removed from the container and completely evaporated into a vapor reservoir. From this container, mass spectrometer inlet reservoirs designated as A and B were twice filled simultaneously, as given by arabic numerals, 1 and 2. The limits designated by "a" are for the deviations from the average of the analyses of the vapor in A and in B.

The deviations from the average in each single column represent the reproducibility of the instrument alone. The deviations between 1 and 2 represent reproducibility plus errors in sampling the vapor reservoir. The over-all spread under the roman numerals includes in addition the lack of uniformity in liquid sampling.

The impurities in tank helium from three Government owned plants are shown in table 11.

TABLE 11.—*Helium from various helium plants*

OTIS, KANS.	
Impurities	Mole percent
Hydrogen	0.67±0.01
Nitrogen	1.43± .02
Total	2.10± .02
EXELL, TEX.	
Hydrogen	0.36±0.02
Nitrogen	1.64± .01
Total	2.00± .02
NAVAJO, N. MEX.	
Hydrogen	0.70±0.03
Nitrogen	1.56± .03
Total	2.26± .03

The presence of hydrogen was completely unsuspected; it was later confirmed, however, by chemical tests. It was thought at first that the hydrogen might have come from the steel storage cylinders, but helium from glass cylinders contained the same percentage of impurities. An analysis of the natural gas showed a trace of hydrogen; apparently it was concentrated along with the helium in the purification process.

The composition of the natural gas from which Texas helium is obtained is shown in table 12.

TABLE 12.—*Natural gas*

Component	Mole percent
Hydrogen	Trace [a]
Helium	2.24 ±0.02
Neon	.12 ± .01
Nitrogen	23.60 ± .05
Argon	.18 ± .01
CO_2	.52 ± .05
Oxygen	.01 ± .005
Methane	66.16 ± .02
Ethane	3.61 ± .02
Propane	2.17 ± .02
n-Butane	.85 ± .01
Pentanes	.36 ± .02
Hexanes	.07 ± .02
Heptanes and higher	.04 ± .02
Total	100

[a] Maximum less than 0.05 mole percent.
[b] Limits represent deviation from average of 2 independent analyses.

It is interesting to note that the neon to nitrogen ratio is appreciably higher than that found in the atmosphere, whereas the argon to nitrogen ratio is slightly lower.

The analysis of a special gas test mixture is shown in table 13. Four independent analyses were made by two computers. The sample was also analyzed by the Gas Chemistry Section of the Bureau.

TABLE 13.—*Gas mixture analyses*

Component	Mass spectrometer (mole percent)					Gas section (mole percent)
	T574	D582	D588	T589	Average	
O_2	0.44	0.43	0.44	0.42	0.43 ±0.01	0.37 ±0.04
CO_2	6.89	6.94	6.83	6.83	6.87 ± .07	6.95 ± .02
N_2	82.06	82.82	82.97	82.46	82.5 ± .05	82.99 ± .02
Argon	.99	.99	1.01	.98	.99 ± .02	----------
Neon	.14	.06	.13	.12	.11 ± .04	----------
CO	9.24	8.57	8.31	8.89	8.8 ± .5	9.41 ±0.05
CH_4	.08	.11	.10	.09	.10 ± .02	.20 ± .02
C_2H_4	.06	.05	.07	.06	.06 ± .01	Unsaturated
C_2H_6	.02	.03	.03	.06	.04 ± .02	0.0 ±0.02
H_2	.08	.08	.12	.10	.09 ± .03	.076 ± .002

Two magnet settings were used in taking the record, 0.15 ampere below mass 12 and 0.5 ampere above.

The separation of N_2 and CO is not sharp. This is because the base peak for both gases is 28. Separation must be made, therefore, by using the 14 and 12 peaks. For a 28 peak height of 100.00 the nitrogen 14 and carbon monoxide 12 peaks are 10.28 and 8.50, respectively; these adverse ratios result in a ten-fold magnification of the normal uncertainty.

VI. TYPE OF MATERIALS THAT CAN BE ANALYZED

A sample to be analyzed successfully in the mass spectrometer should have an appreciable vapor pressure at room temperature. Materials having vapor pressures as low as 10^{-4} millimeter have been run in the instrument, but the peaks are too low for precise calculations. (In general, it is preferable that the vapor pressure exceed 1 millimeter for direct analyses.) A method will be described in succeeding articles by which the analyses of rubbers, plastics, and materials having no appreciable vapor pressure can be performed.

The chemical composition of the material to be analyzed is of little consequence. For the sake of longevity of the filament it is desirable to keep water vapor low although samples saturated with water vapor at atmospheric pressure are regularly tested. Gas mixtures containing small amounts of PH_3, H_2S, SO_2, and chlorinated and fluorinated hydrocarbons offer no difficulty.

The most difficult materials to separate are the stereoisomers. The cracking patterns for *cis*- and *trans*-butene-2 are given in table 1. The fragmentation ratios are very close, the greatest difference being for mass 29. The 58:29 mass ratios are sufficient to give a 1-percent separation in a mixture of pure butene-2. In a hydrocarbon mixture, however, a separation of better than 2 percent cannot be expected, even under favorable conditions. The cracking patterns for all the pentenes have not been worked out.

The range of masses that can be resolved in the instrument covers all masses up to 150 for the slit settings ordinarily used. The isotopes of mercury can be distinguished but resolution is not complete. In the analyses of hydrocarbons resolution above 150 is not essential, as the sensitivity can be determined from any lower peak of sufficient size, and the pattern can be taken from any series of carbon groups on the record. The analyses of heavy hydrocarbons is limited more by vapor pressure than by mass.

VII. ACCURACY OF ANALYSES

A survey of some 1,700 determinations that have been run up to the present time leads to the conclusion that the precision of the mass spectrometer is high. Duplicate determinations in general check to within a few tenths to a few thousandths of 1 percent, the usual deviation being a few hundredths of 1 percent.

The absolute accuracy, in contrast, is not easy to determine. A large number of determinations have been compared with the freezing-point method. Agreements to within the limits of reproducibility have been obtained in every instance except one, in which case the container from which the sample was withdrawn was nearly

empty. These results are not to be generalized, as freezing-point measurements can be made only on nearly pure materials.

A number of checks have been made against synthetic mixtures and with mixtures analyzed by chemical methods, and agreements to within a few tenths of 1 percent have been obtained. Such results, however, cannot be used to define the accuracy, as in no case was the composition known to be within the limits of deviation. It is obvious that the limits of accuracy should not be defined by occasional extreme cases of agreement or disagreement.

Errors in analysis enter from three different sources: (1) the instrument, (2) the sample, and (3) the computations.

The problem of obtaining a representative sample is far from simple. The principal source of instrumental error results from a time-to-time variation in the sensitivity, or the cracking pattern or both. The effect of these variations can be largely overcome by checking the pattern and sensitivity for the most abundant constituents in the mixture being tested and then correcting the patterns and sensitivities of the other constituents proportionally. Thus, in the analysis of butadiene, the pattern error can be rendered negligible by running pure butadiene every day and correcting the patterns of all the other constituents therefrom. It should be pointed out that a daily check on the pattern is not imperative except in obtaining the precision reported in this paper.

Instrumental errors may also enter through fractionation in the gas-inlet leak. When capillary leaks are used, fractionation errors may be large; in the special leak used on the instrument this source of error is reduced to negligible proportions.

Errors in computation, may enter through the use of incorrect patterns and sensitivities for the various constituents in the sample and through an improper interpretation of the pattern for the mixture.

For the most part, instrumental errors are manifest by lack of reproducibility between duplicate analyses, whereas computational, errors are indicated by the magnitude of the residuals, such as those shown in the last column of table 3.

In view of the number and nature of the various contributing factors involved, it is impossible to define the accuracy of a result obtained with the mass spectrometer by any given set of limits. In the analyses given in this report there is sufficient reason to believe that the absolute accuracy is very close to the limits of reproducibility. Analyses have been made, however, that contained mistakes in judgment in interpreting the mixture pattern, and in which incorrect calibrating patterns were used. In these instances the residuals were usually large.

In general, it can be stated that when the residuals are small the limits of accuracy are of the same order of magnitude as the limits of reproducibility, and when the residuals are large the limits of accuracy may be correspondingly large.

The authors are indebted to H. W. Bond for preparing many of the hydrocarbons used as standards, to Dorothy Thompson and Laura Edmundson for making many of the computations shown, and to O. L. Parham for operating the mass spectrometer.

WASHINGTON, June 12, 1945.

654385—45——3

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1665

Part of Journal of Research of the National Bureau of Standards, Volume 35, August 1945

HEATS OF COMBUSTION AND ISOMERIZATION OF THE EIGHT C_9H_{12} ALKYLBENZENES

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ABSTRACT

The heats of isomerization of the eight C_9H_{12} alkylbenzenes were determined by measurement of the ratios of the heats of combustion in the liquid state of purified samples of these compounds by the procedure previously described for the hexanes, heptanes, and octanes. The data yield the following values for the heat of isomerization in the liquid state at 25° C, $\Delta H°$, of *n*-propylbenzene into each of the C_9H_{12} alkylbenzenes, in kilocalories per mole: *n*-propylbenzene, 0.00; isopropylbenzene, -0.67 ± 0.16; 1-methyl-2-ethylbenzene, -1.93 ± 0.16; 1-methyl-3-ethylbenzene, -2.48 ± 0.19; 1-methyl-4-ethylbenzene, -2.74 ± 0.26; 1,2,3-trimethylbenzene, -4.83 ± 0.22; 1,2,4-trimethylbenzene, -5.61 ± 0.16; 1,3,5-trimethylbenzene, -6.00 ± 0.26. These data were combined with the value previously reported for the heat of combustion of *n*-propylbenzene to obtain values for the heats of combustion of each of the C_9H_{12} alkylbenzenes in the liquid state at 25° C.

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I. INTRODUCTION

In continuation of the program of determining the heats of combustion, formation, and isomerization of hydrocarbons of various types [1, 2, 3, 4],[1] calorimetric measurements have been made that yield values for the differences in the heats of combustion, or the heats of isomerization, of the eight C_9H_{12} alkylbenzenes in the liquid state at 25° C. These heats of isomerization are combined with the values previously reported for the heat of combustion of *n*-propylbenzene [3] to obtain values for the heats of combustion of each of the C_9H_{12} alkylbenzenes in the liquid state at 25° C.

[1] Figures in brackets indicate the literature references at the end of this paper.

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, UNCERTAINTIES

The unit of energy upon which the values reported in this paper are based is the international joule, derived from mean solar seconds and from the units of international ohms and international volts in terms of which certification of standards of resistance and electromotive force is made by the National Bureau of Standards. For conversion to the conventional thermochemical calorie, the following relation is used [5]:

1 calorie=4.1833 international joules.

The molecular weight of carbon dioxide, the mass of which was used to determine the amount of reaction, was taken as 44.010, from the 1941 table of atomic weights [6].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [7].

Definitions of the symbols used are given in the previous papers [1, 2, 3, 4].

III. METHOD AND APPARATUS

The same method and apparatus were used in the present investigation as in the work on the hexanes [1], heptanes [2], and octanes [4], with the exception that a chronograph was used to record the time during the first 5 minutes of the reaction period. The chronograph had two pens, one recording seconds and the other the taps of a telegraph key. The telegraph key was tapped when the resistance of the platinum resistance thermometer in the calorimeter passed certain previously selected values.

IV. MATERIALS

The compounds used in the present investigation were samples from the API–NBS series of highly purified hydrocarbons, which are being prepared through a cooperative undertaking of the American Petroleum Institute and the National Bureau of Standards. A complete description of the purification and determination of the purity of these compounds will appear in other reports [8, 9]. The amounts of impurity in these samples, as determined from measurements of freezing points made by A. R. Glasgow, Jr., E. T. Murphy, and A. J. Streiff, at this Bureau, were as follows: *n*-Propylbenzene, 0.0029 ±0.0008; isopropylbenzene, 0.0005 ±0.0002; 1-methyl-2-ethylbenzene, 0.0024 ±0.0007; 1-methyl-3-ethylbenzene, 0.0022 ±0.0015; 1-methyl-4-ethylbenzene, 0.0005 ±0.0002; 1,2,3-trimethylbenzene, 0.0008 ±0.0004; 1,2,4-trimethylbenzene, 0.0036 ±0.0020; 1,3,5-trimethylbenzene, 0.0007 ± 0.0003, mole fraction [8, 9].

As the manner of purification of these compounds [8, 9] was such as to leave substantially only close-boiling isomeric impurities in the respective compounds, it is calculated that in the worst case the measured heat of combustion would be affected by less than 0.002 percent because of impurities in the compound.

V. RESULTS

The experimental results of the present investigation are summarized in table 1, which gives for each of the eight compounds the following data: The number of experiments performed; the minimum and

TABLE 1.—*Results of the calorimetric combustion experiments*

TABLE 1.—*Results of the calorimetric combustion experiments*

Compound (liquid)	Number of experiments	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_a	B	
									Mean	Standard deviation of mean
		g	min^{-1}	Ohm	Ohm	Ohm	Ohm	Ohm	$Ohm/g\ CO_2$	$Ohm/g\ CO_2$
n-Propylbenzene	6	2.24788 to 3.08660	0.001962 to .001989	0.001055 to .003260	0.000304 to .000520	0.216719 to .297432	0.000416 to .000429	0.000006 to .000008	0.0962420	±0.0000061
Isopropylbenzene	7	2.83771 to 3.12459	.001959 to .001979	.001052 to .001871	.000350 to .000462	.273359 to .300887	.000399 to .000427	.000004 to .000007	0.0961908	±.0000024
1-Methyl-2-ethylbenzene	5	3.20071 to 3.67189	.001969 to .001980	.000988 to .001029	.000270 to .000283	.307039 to .353211	.000409 to .000421	.000004 to .000008	0.0960945	±.0000020
1-Methyl-3-ethylbenzene	7	2.83024 to 3.43990	.001970 to .001982	.000439 to .002043	.000264 to .000315	.272265 to .330713	.000413 to .000431	.000004 to .000007	0.0960510	±.0000046
1-Methyl-4-ethylbenzene	7	3.01930 to 3.24697	.001954 to .001961	.000767 to .001505	.000240 to .000352	.290443 to .311654	.000409 to .000423	.000004 to .000007	0.0960313	±.0000085
1,2,3-Trimethylbenzene	6	2.91747 to 3.39652	.001971 to .001985	.000932 to .001620	.000289 to .000390	.280049 to .329051	.000419 to .000427	.000004 to .000007	0.0958698	±.0000062
1,2,4-Trimethylbenzene	5	3.09067 to 3.32189	.001973 to .001984	.000551 to .001084	.000325 to .000403	.296058 to .318221	.000410 to .000422	.000004 to .000005	0.0958099	±.0000025
1,3,5-Trimethylbenzene	6	2.65851 to 3.43334	.001970 to .001980	.000147 to .002285	.000320 to .000389	.254702 to .328815	.000414 to .000420	.000004 to .000006	0.0957790	±.0000086

maximum values of the mass of carbon dioxide formed in the combustion and of the calorimetric quantities k, K, U, ΔR_c, Δr_t, Δr_n [1]; the mean value of B, and its standard deviation, in ohms per gram of carbon dioxide formed, as defined by equation 4 of reference [1]. The symbols in table 1 have the same significance as in the previous report [1] and the references there cited.

In table 2 are given, for the eight C_9H_{12} alkylbenzenes, values of the following: The constant B in ohms per gram of carbon dioxide, as given in table 1; B°, which is B corrected to the ideal bomb reaction by the method of Washburn [10];[2] B_i°/B_n°, which is equal to the ratio of the heat evolved, per mole of hydrocarbon, in the ideal bomb process at 28° C for each isomer to that of *n*-propylbenzene; $(-\Delta U_R^\circ)_n-(-\Delta U_R^\circ)_i$, the difference, between *n*-propylbenzene and each isomer, in the heat of combustion in the ideal bomb process at 28° C; H_i° (liquid)$-H_n^\circ$ (liquid), the heat of isomerization of *n*-propylbenzene into each isomer, at 25° C and 1 atmosphere, for the liquid state; and $-\Delta Hc^\circ$, the decrement in heat content accompanying the reaction of combustion of the hydrocarbon in the liquid state in oxygen to form gaseous carbon dioxide and liquid water, with all the reactants and products in their thermodynamic standard states at 25° C. The value of the heat of isomerization was obtained by means of the relation [1]:

$$(-\Delta U_R^\circ)_n-(-\Delta U_R^\circ)_i=(-\Delta U_R^\circ)_n\,(1-B_i^\circ/B_n^\circ) \qquad (1)$$

For this calculation, the value of $(-\Delta U_R^\circ)_n$ at 28° C was taken as 5209.2 int. kj/mole [3]. The value for the heat of combustion of a given isomer was obtained by appropriately combining the heat of isomerization with the heat of combustion of *n*-propylbenzene as given by the equations:

$$C_9H_{12}\ (n\text{-propylbenzene, liquid})+12O_2\ (\text{gas})=9\ CO_2\ (\text{gas})+6H_2O\ (\text{liquid}). \qquad (2)$$

$$\Delta H^\circ_{298.16}=-5217.37\pm0.68\ \text{int. kj/mole}=-1247.19\pm0.16\ \text{kcal/mole}. \qquad (3)$$

The experimental data of the present and the previous investigations on the alkylbenzenes [3] are being compared with the data of earlier investigations in a report [11] that will include selected "best" values for the heats of combustion and formation, for both the liquid and gaseous states, at 25° C, of all the isomeric alkylbenzenes through $C_{11}H_{16}$ with general formulas for calculating values for the higher alkylbenzenes.

[2] The Washburn correction is the same for all these compounds as they are isomers, but account is taken of the variation of the Washburn correction with amount of sample burned. As used here, the Washburn correction was modified to apply to 28° C and to the gases at zero pressure (instead of 1 atmosphere).

TABLE 2.—*Heats of isomerization and combustion in the liquid state*

TABLE 2.—*Heats of isomerization and combustion in the liquid state*

Compound (liquid)	B at 28.00° C	B° at 28.00° C	Ratio of the heats of combustion in the ideal bomb process, B°_i/B°_a, at 28.00° C	Difference in the heats of combustion in ideal bomb process, $(-\Delta U^\circ_B)_a - (-\Delta U^\circ_B)_i$, at 28.00° C	Heat of isomerization of the liquid, $H^\circ_{a(liq)} - H^\circ_{a(liq)}$, at 25.00° C		Heat of combustion, $-\Delta H^\circ_c$, at 25.00° C	
	Ohm/g CO_2	*Ohm/g* CO_2		*Int. kj/mole*	*Int. kj/mole*	*kcal/mole*	*Int. kj/mole*	*kcal/mole*
n-Propylbenzene	0.0962420±0.0000122	0.0962016±0.0000122	1.000000	0.00	0.00	0.00	5217.37±0.68	1247.19±0.16
Isopropylbenzene	.0961908± .0000048	.0961498± .0000048	.999462±0.000131	2.80±0.68	−2.80±0.68	−0.67±0.16	5214.57± .96	1246.52± .23
1-Methyl-2-ethylbenzene	.0960945± .0000040	.0960523± .0000040	.998448± .000128	8.08± .67	−8.08± .67	−1.93± .16	5209.29± .95	1245.26± .23
1-Methyl-3-ethylbenzene	.0960510± .0000092	.0960097± .0000092	.998005± .000153	10.39± .80	−10.39± .80	−2.48± .19	5206.98±1.05	1244.71± .25
1-Methyl-4-ethylbenzene	.0960313± .0000170	.0959900± .0000170	.997800± .000209	11.46±1.09	−11.46±1.09	−2.74± .26	5205.91±1.28	1244.45± .31
1,2,3-Trimethylbenzene	.0958698± .0000124	.0958287± .0000124	.996124± .000174	20.19± .91	−20.19± .91	−4.83± .22	5197.18±1.14	1242.36± .27
1,2,4-Trimethylbenzene	.0958099± .0000050	.0957683± .0000050	.995496± .000132	23.46± .69	−23.46± .69	−5.61± .16	5193.91± .97	1241.58± .23
1,3,5-Trimethylbenzene	.0957790± .0000172	.0957380± .0000172	.995181± .000211	25.10±1.10	−25.10±1.10	−6.00± .26	5192.27±1.29	1241.19± .31

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WASHINGTON, April 3, 1945.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1666

Part of Journal of Research of the National Bureau of Standards, Volume 35, August 1945

THIN-WALLED ALUMINUM BETA-RAY TUBE COUNTERS

By Burrell W. Brown and L. F. Curtiss

ABSTRACT

A description is given of aluminum-tube Geiger-Müller counters having a wall thickness of 0.004 inch and constructed from commercially available tooth-paste tubes. These tubes as furnished are in the hard temper and have uniform wall thickness, which enable them to stand complete evacuation without a tendency to collapse. By copperplating the aluminum it is possible to soft-solder fittings to the tube to construct a counter that can be permanently sealed after filling and that will maintain its characteristics over a long period. The procedure reduces the cost of making this type of counter, as the aluminum tubes are inexpensive, and very simple operations are required in the construction of the counters.

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I. INTRODUCTION

An economical method of making thin-walled aluminum Geiger-Müller counter tubes for the measurement of beta rays would greatly increase the usefulness of this type of instrument in the field of radioactivity. Present methods require, the boring of metal tubes or rods [1] to a thin wall. This is a delicate and expensive operation, and the thinnest walls obtainable are approximately 0.007 inch. Thin-walled counters have also been made by drawing glass tubing to a thin-walled section and silvering the inside.[2] This procedure does not give a very uniform wall, which is usually of a thickness greater than that corresponding to 0.007-inch aluminum. Other methods require the use of wax seals, which do not yield tubes of very long life as the organic vapors commonly used in filling counters attack most waxes.

II. THIN-WALLED ALUMINUM TUBES

It has recently been noted that thin-walled aluminum tubes quite suitable for the construction of counters are commercially available. A typical tube is ⅝ inch in diameter and 4½ inches long, with walls 0.0044 ± 0.0004 inch in thickness. The walls are uniform throughout

[1] J. R. Dunning and S. M. Skinner, Rev. Sci. Instr. **6**, 243 (1935); J. Halpern and O. C. Simpson, **8**, 172 (1937).

[2] A. H. Barnes, Rev. Sci. Instr. **7**, 107 (1936); J. C. Wang, J. F. Marvin, and K. W. Stenstrom **13**, 81 (1942).

the length and circumference within the limits indicated. These tubes are made in quantity as containers for such materials as tooth-paste and are furnished with one end fitted with the conventional screw cap and the opposite end open to the full diameter of the tube. Made by mass-production methods these tubes are inexpensive and of very uniform dimensions, and therefore are suitable as a component of a beta-ray counter. They are in the hard temper, which enables them to withstand complete evacuation with no tendency to collapse.

III. COPPERPLATING THE ALUMINUM TUBE

It is of advantage to construct counters that can be filled and sealed permanently so that they will maintain their characteristics over considerable periods of time. This requires the elimination of wax seals, gaskets, and similar arrangements. To accomplish this with the aluminum-tube counters, it has been found desirable to plate the aluminum with copper to permit the use of soft solder in joining the parts. There are several methods by which an adherent plating of copper can be applied to aluminum. For the benefit of those who may desire to construct such counters, the method of plating found most convenient is described.

The first step is to clean the aluminum surfaces to be plated in a strong solution of potassium hydroxide, immersing the aluminum until a smooth film of water will spread over it uniformly, indicating that the aluminum surface is clean. The next step is to anodize the aluminum surface. After rinsing all the potassium hydroxide solution from the aluminum, it is used as an electrode in a solution of 10- to 15-percent oxalic acid to produce an anodic film on the surface. It is convenient to anodize two pieces together by using them as electrodes connected to the alternating-current supply through a variable-voltage transformer. Initially, the voltage applied should be of the order of 1 or 2 volts, and this may be increased to around 50 volts as the anodic film develops. Care should be taken to hold the voltage low enough at all times to avoid heating of the solution by the current. After 15 to 20 minutes the aluminum is removed, rinsed in cold water, and etched for a few seconds in a 1-percent hydrofluoric acid solution until a slight evolution of gas is apparent. It is then immediately rinsed in cold water, and the surface is ready for plating. The usual copper sulfate solution, to which a small amount of sulfuric acid has been added, is used for plating. The plating of a layer of copper a few thousandths of an inch in thickness requires about 20 minutes. In constructing the counters, both ends of the tubes are plated with copper. If copper is deposited over a larger area than is desired, the excess may be removed at any time by etching with strong nitric acid, which has little effect on the aluminum.

The etching of the anodic coating with hydrofluoric acid may be eliminated if care is taken to develop a thin coating in the anodizing process. The proper thickness is obtained by interrupting the anodizing process when the potential reaches about 2 volts. Some difficulty may be encountered in determining the proper conditions to secure an adherent coating of copper by use of this alternative method.

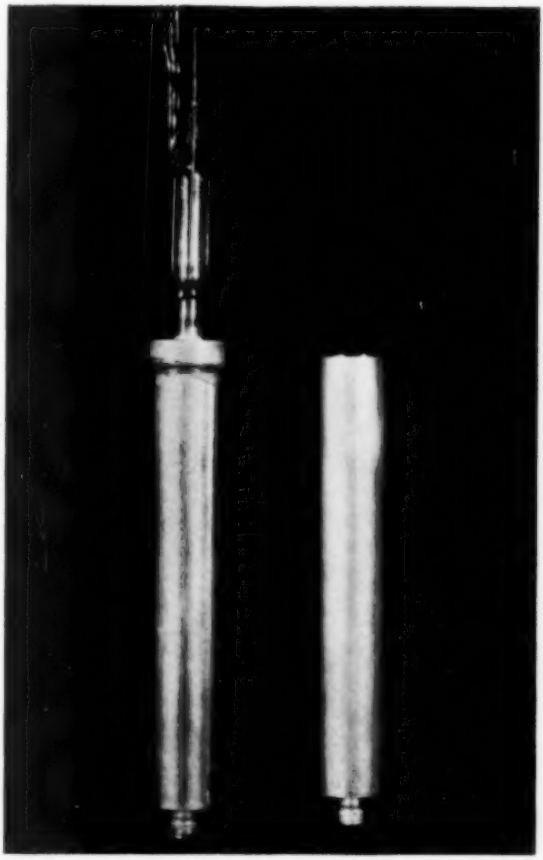

FIGURE 3.—*Completed counter.*

IV. CONSTRUCTION OF THE GEIGER-MÜLLER COUNTER

The assembly of the counter is shown in cross section in figure 1. The circular end of the tooth-paste tube, *T*, is closed by the copper bushing, *B*, which is soft soldered to the plated aluminum tube, as indicated. The bushing is fitted with a ¼-inch Kovar tube, *K*, silver-soldered in an axial hole, as shown. A short glass tube sealed to *K* provides a support for one end of the central wire, *W*, and also carries a side tube for evacuating, filling, and sealing the counter. The glass tube is continued inside of *K* to form a sleeve around the central wire. The opposite end of the aluminum tube is closed by a copper plug, *P*, soldered into the small tubular opening of the tube. The plug is drilled to take a small piece of Kovar wire, which carries a glass bead, *G*, to serve as a support for the central wire at this end. The plug and wire are soft soldered in one operation to the aluminum tube, previously copperplated at this point.

The order of assembly found convenient is first to silver solder tube *K* into copper bushing, *B*. The glass tubing is then sealed into *K* and the bushing, *B*, soft soldered into tube, *T*. The central wire system is then made up and lowered into *T* to protrude through the screw-cap end. Copper plug, *P*, is soft soldered to the short Kovar wire and then into *T*. The Kovar wire, *R*, is then pulled into position at the opposite

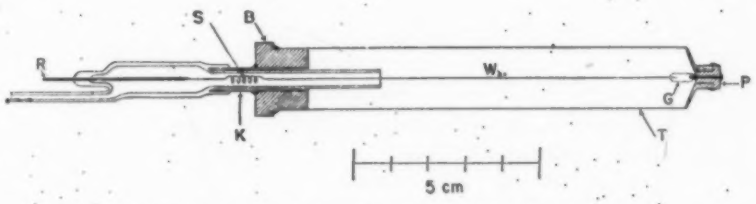

FIGURE 1.—*Cross section of assembly of counter.*

end and sealed into the glass. The dimensions are such that there is a moderate tension on the spring, *S*. If the dimensions are carefully chosen this spring may be eliminated.

The performance of the finished counter depends, of course, on the type of filling used. In the counter described here, the usual alcohol-argon mixture has been found to yield plateaus and thresholds similar to other types of Geiger-Müller counters containing this mixture. A slope of 0.1 percent per volt is readily obtained. A curve showing the variation of counting rate with voltage applied to the counter is shown in figure 2. This curve is maintained for several months, which is as long as the counters were under observation. Experience indicates that a counter will leak occasionally as a result of imperfect soldering. This can be quickly repaired. In a few cases it was also found that the aluminum tooth-paste tubes have a small leak, probably due to pin holes. Perhaps 5 percent of the tubes may have this defect, which can be detected by preliminary evacuation.

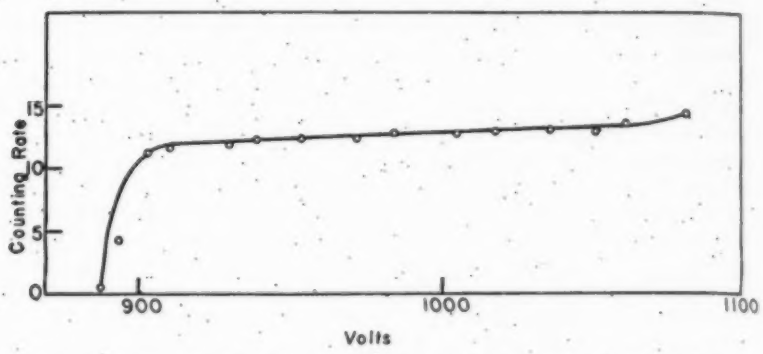

FIGURE 2.—*Variation of counting rate with voltage applied to counter.*

A completed counter, ready for filling, and an empty tube are shown in figure 3. Aluminum tubes of other diameters but of approximately the same wall thickness and that do not collapse on evacuation are also available commercially.

WASHINGTON, May 4, 1945.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1667

Part of Journal of Research of the National Bureau of Standards, Volume 35, August 1945

METHOD OF LAGRANGIAN CURVILINEAR INTERPOLATION[1]

By William J. Taylor[2]

ABSTRACT

This report describes a simplified method of computing Lagrangian coefficients for curvilinear interpolation, which may be used when tables of Lagrangian coefficients are not available or when tables are available but the coefficients are not tabulated for the exact fraction of the interval to which the interpolation is to be made.

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I. INTRODUCTION

The common formulas of curvilinear interpolation,[3] such as those of Newton, Gauss, Stirling, Bessel, and Lagrange[4] when carried to completion, are all equivalent in that they approximate the function by a polynomial of suitable degree (the number of points required is one greater than the degree of the polynomial assumed). All of these formulas except that of Lagrange require, as a first step, the computation of a "table of differences" for the function, to an order equal to the degree of the polynomial. Lagrangian interpolation, on the other hand, is carried out by multiplying each of the tabulated values on which the interpolation is to be based by a suitable coefficient—the Lagrangian coefficients—and taking the sum of these products. This "cumulative" multiplication can be carried out as a continuous operation on a modern calculating machine, and when such a machine is available Lagrangian interpolation is usually more rapid than the other methods referred to.

Very extensive tables of Lagrangian interpolation coefficients are now available[5] (references to other, less complete, tables are given in this work).

[1] This investigation was performed at the National Bureau of Standards as part of the work of the American Petroleum Institute Research Project 44 on the "Collection and Analysis of Data on the Properties of Hydrocarbons."

[2] Research Associate on the American Petroleum Institute Research Project 44 at the National Bureau of Standards.

[3] The discussion in this report is restricted to interpolation in tables in which a function is tabulated at equally spaced intervals of the independent variable.

[4] David, Gibb, Edinburgh Mathematical Tracts No. 2, Interpolation and numerical integration (G. Bell & Sons, Ltd., London, 1915).

[5] Tables of Lagrangian interpolation coefficients, Mathematical Tables Project, Works Project Administration, Federal Works Agency. (National Bureau of Standards; Columbia University Press, New York, N. Y., 1944).

In this report there is described a simplified method of computing the Lagrangian coefficients, which may be used when tables of Lagrangian coefficients are not available, or when tables are available, but the coefficients are not tabulated for the exact fraction of the interval to which the interpolation is to be made. This method requires only a single division for the computation of each coefficient, for interpolation on the basis of any number of tabulated values. The coefficients, as thus computed, are not normalized—they may be normalized in the usual way, although it is usually more convenient to interpolate by means of the non-normalized Lagrangian coefficients.

Lagrangian interpolation, with the use of tables of Lagrangian coefficients (see footnote 5), or by the method described in this report, is recommended as a rapid and generally useful method of interpolation in those tables in which a function, or property, is tabulated at several equally spaced values of the independent variable. The number of tabulated values, or the degree of the polynomial, on which the interpolation is based must be chosen to represent the function with sufficient accuracy in the interval in question.

II. GENERAL METHOD

The form of the modified Lagrangian interpolation formula will be stated, and then the derivation of the formula will be given.

Let the $(n+1)$ tabulated values of the function $y(x)$ on which the interpolation is to be based be $y_0, y_1, \ldots, y_k, \ldots, y_n$, and let the corresponding values of the independent variable—equally spaced at intervals of h — be $x_0, x_1, \ldots, x_k, \ldots, x_n$. The $(n+1)$ values of y determine a polynomial of the nth degree in x, $P(x)$, which is an approximation to the function $y(x)$ in the range x_0 to x_n. The value of $P(x)$, and therefore, approximately, of y, at a given value of x, is given by the modified Lagrangian formula

$$P(x)=\sum_{k=0}^{n} a_k y_k / \sum_{k=0}^{n} a_k, \tag{1}$$

where the coefficients, a_k, are given by

$$a_k=\pm\binom{n}{k}/|(x_k-x)/h|. \tag{2}$$

$|(x_k-x)/h|$ is the absolute value of $(x_k-x)/h$, and $\binom{n}{k}$ is the binomial coefficient

$$\binom{n}{k}=n!/k!(n-k)!. \tag{3}$$

The signs of the coefficients, a_k, are determined as follows: If x lies between x_m and x_{m+1},

$$x_m<x<x_{m+1},$$

hen the coefficients, . . ., a_{m-2}, a_m, a_{m+1}, a_{m+3}, . . ., are positive, and he coefficients, . . ., a_{m-3}, a_{m-1}, a_{m+2}, a_{m+4}, . . ., are negative. The attern of signs is thus of the type

$$- \quad + \quad - \quad + \quad - \quad + \quad + \quad - \quad + \quad - \quad + \quad - \quad . \; . \; .$$

POINT OF INTERPOLATION

The coefficients, a_k, are proportional to the Lagrangian interpolation oefficients but are not normalized. In fact, the sum of the a_k's is iven by the expression

$$\sum_{k=0}^{n} a_k = n! \Big/ \prod_{k=0}^{n} |(x_k - x)/h|, \tag{4}$$

which may be used as a check on the calculation of the a_k's.

If several interpolations to the same fraction of an interval are to e made, it is more convenient to put eq 1 in the form

$$P(x) = \sum_{k=0}^{n} A_k y_k, \tag{5}$$

where the A_k's are the normalized Lagrangian coefficients,

$$A_k = a_k \Big/ \sum_{k=0}^{n} a_k, \tag{6}$$

which have been tabulated elsewhere (see footnote 5). As used here, "normalized" indicates that the algebraic sum of the coefficients s unity.

These results may be derived in the following way: $P(x)$ may be written in the form

$$P(x) = \sum_{k=0}^{n} \left[\frac{(x-x_0)(x-x_1) \; . \; . \; . \; (x-x_{k-1})(x-x_{k+1}) \; . \; . \; . \; (x-x_n)}{(x_k-x_0)(x_k-x_1) \; . \; . \; . \; (x_k-x_{k-1})(x_k-x_{k+1}) \; . \; . \; . \; (x_k-x_n)} \right] y_k \tag{7}$$

s $P(x)$ (by definition) and the expression on the right of eq 7 are both polynomials of the nth degree in x, and are equal to y_k when $x = x_k$, for $k = 0, 1, \ldots, n$. But two polynomials of the nth degree which oincide at $(n+1)$ points must be identical, which establishes eq 7. Rearrangement of eq 7 yields

$$P(x) =$$

$$\left[\left(\frac{x-x_0}{h} \right) \left(\frac{x-x_1}{h} \right) \; . \; . \; . \; \left(\frac{x-x_n}{h} \right) \Big/ n! \right] \sum_{k=0}^{n} \left[n! \Big/ \left(\frac{x_k-x_0}{h} \right) \left(\frac{x_k-x_1}{h} \right) \; . \; . \; . \right.$$

$$\left. \left(\frac{x_k-x_{k-1}}{h} \right) \left(\frac{x_k-x_{k+1}}{h} \right) \; . \; . \; . \; \left(\frac{x_k-x_n}{h} \right) \right] y_k \Big/ \left(\frac{x-x_k}{h} \right) \tag{8}$$

The expression in brackets under the summation sign is equal in absolute value to the binomial coefficient, $\binom{n}{k}$. Therefore if the signs of the terms are temporarily disregarded, as indicated by the $\pm$ sign, eq 8 may be rewritten as

$$P(x)=\left[\frac{1}{n!}\prod_{k=0}^{n}\left|(x-x_k)/h\right|\right]\sum_{k=0}^{n}\left[\pm\binom{n}{k}\Big/\left|(x_k-x)/h\right|\right]y_k. \tag{9}$$

Inspection of eq 7 shows that the signs of the terms follows the rule already given for the signs of the coefficients a_k. In view of the definition of a_k, eq 2, therefore, eq 9 becomes

$$P(x)=\left[\frac{1}{n!}\prod_{k=0}^{n}\left|(x-x_k)/h\right|\right]\sum_{k=0}^{n}a_k y_k. \tag{10}$$

In the special case in which $y_k=1$, for $k=0, 1, \ldots, n$, the polynomial $P(x)$ must have the value unity for all values of x. It follows that

$$\left[\frac{1}{n!}\prod_{k=0}^{n}\left|(x-x_k)/h\right|\right]\sum_{k=0}^{n}a_k=1. \tag{11}$$

Equations 10 and 11 lead immediately to eq 1, and eq 11 is equivalent to eq 4.

III. NUMERICAL EXAMPLE

Given the following (equally spaced) values of the descending exponential function, e^{-x}, find by interpolation the value of e^{-x} at $x=0.54316$:

x	$y=e^{-x}$
$x_0=0.52$	$y_0=0.594\ 520\ 548\ 0$
$x_1=0.53$	$y_1=0.588\ 604\ 969\ 7$
$x_2=0.54$	$y_2=0.582\ 748\ 252\ 4$
$x_3=0.55$	$y_3=0.576\ 949\ 810\ 4$
$x_4=0.56$	$y_4=0.571\ 209\ 063\ 8$

Solution: The interval, h, of the independent variable, x, is 0.01. The values of the binomial coefficients for $n=4$ are 1, 4, 6, 4, and 1. The value $x=0.54316$ lies between $x_2=0.54$ and $x_3=0.55$. Then the values of the a_k's, or the non-normalized Lagrangian coefficients, are given by eq 2:

$$\begin{aligned}
a_0&=+\binom{4}{0}/\left|(x_0-x)/h\right|=+1/2.316=+\ 0.431\ 778\ 9\\
a_1&=-\binom{4}{1}/\left|(x_1-x)/h\right|=-4/1.316=-\ 3.039\ 513\ 7\\
a_2&=+\binom{4}{2}/\left|(x_2-x)/h\right|=+6/0.316=+18.987\ 341\ 8\\
a_3&=+\binom{4}{3}/\left|(x_3-x)/h\right|=+4/0.684=+\ 5.847\ 953\ 2\\
a_4&=-\binom{4}{4}/\left|(x_4-x)/h\right|=-1/1.684=-\ 0.593\ 824\ 2\\
\hline
\sum_{k=0}^{4}a_k&=21.633\ 736\ 0
\end{aligned}$$

A check may be obtained from eq 4:

$$4!\Big/\prod_{k=0}^{4}|(x_k-x)/h| = 24/(2.316)(1.316)(0.316)(0.684)(1.684)$$

$$= 21.633\ 736\ 0.$$

The value of $P(x)$ at $x=0.54316$ may now be calculated from eq 1 (the cumulative multiplication involved may be performed as a continuous operation on the calculating machine):

$$P(x) = \sum_{k=0}^{4} a_k y_k \Big/ \sum_{k=0}^{4} a_k$$

$$= \left(\frac{12.567\ 246\ 5}{21.633\ 736\ 0}\right)$$

$$= 0.580\ 909\ 673.$$

The true value of $y=e^{-x}$, at $x=0.54316$, correct to 10 decimal places, is

$$y = 0.580\ 909\ 674\ 4.$$

When the same coefficients are to be used several times, it is convenient to compute the normalized Lagrangian coefficients, or the A_k's, from eq 6:

$$\begin{aligned} A_0 &= +0.019\ 958\ 592 \\ A_1 &= -\ .140\ 498\ 789 \\ A_2 &= +\ .877\ 672\ 807 \\ A_3 &= +\ .270\ 316\ 380 \\ A_4 &= -\ .027\ 448\ 990 \\ \hline \sum_{k=0}^{4} A_k &= \ \ 1.000\ 000\ 000 \end{aligned}$$

These coefficients differ by one or two units in the last place from the correct values (see p. 232 of the reference in footnote 5) because the a_k's were computed to only seven decimal places. The value of $P(x)$ at $x=0.54316$ may now be calculated from eq 5:

$$P(x) = \sum_{k=0}^{4} A_k y_k$$

$$= 0.580\ 909\ 674.$$

WASHINGTON, March 3, 1945.